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(54) Title: LAMINATING METHOD AND HOT MELT ADHESIVE**(57) Abstract**

The invention relates to a method of laminating a sheet material, especially a laminating film material, onto a substrate with a hot melt adhesive, by in-line coating said hot melt adhesive onto said sheet material and/or said substrate, at or above the lowest processing temperature of said hot melt, and laminating the sheet material onto said substrate, said hot melt adhesive comprising a thermoplastic polymer selected from copolymers of olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters; copolymers of olefins, especially ethylene, and vinyl compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene; ionomers and corresponding copolymers; and mixtures thereof. The invention further relates to a hot melt laminating adhesive as above indicated, suitable for in-line coating in an in-line lamination process.

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5 Laminating method and hot melt adhesive

The invention is concerned with the field of industrial laminating methods and adhesives suitable for such industrial processes. It relates to a method of laminating a
10 laminating material, especially a laminating film material, to a substrate with a hot melt adhesive, and it relates to a hot melt adhesive which is suitable for practising this method. More specifically, the invention relates to the production of transparent, high-gloss film
15 laminations for printed paper or cardboard items, such as book-covers, picture-postcards, calendars, posters, high quality packaging materials, etc.

In the art, both solvent-based and dispersion adhesives
20 have been used for such laminations. However, solvent-based adhesives will, in the future, increasingly have to be avoided for health and ecological reasons. The use of water based adhesives entails increased energy consumption, and extended, difficult apparatus cleaning
25 procedures. Also, relatively large amounts of water based adhesives have to be applied in industrial laminating processes, and water based adhesives are not fully suitable for all types of printed materials.

30 These problems have partly been solved in the art by the use of solvent-free ("100%") adhesives. Conventionally, such adhesives have been based on liquid reactive polyurethanes. Such adhesives cure under the influence of moisture. For this reason, the laminated articles can not
35 be immediately further processed, since the curing reaction of the adhesive takes time and is generally not finalized after the laminating step. This complicates

the further handling of laminated articles. Also, such reactive polyurethane adhesives contain isocyanates, which are considered as health and environmental hazards. The cleaning problems encountered with prior art water-based dispersion adhesives are also not overcome by such polyurethane adhesives, especially since the adhesives readily cure with humidity when spilt.

As an alternative, laminating adhesives have been used which cure under the influence of ultraviolet light. Such "UV-curing" adhesives can be used in small amounts at high machine speeds. However, machine and plant cleaning problems are comparable to those caused by reactive polyurethane adhesives; frequently, processing machines must be provided with UV-light protection, to prevent curing of spilt adhesive. UV-curing adhesives have the further disadvantages of not being acceptable for food stuff packaging and of producing a typical odor which is quite often extremely disagreeable. Also, these adhesives are not suited for some types of printed articles.

In another alternative approach, film materials are used which are either made of a heat-sealable polymer material, or are pre-coated with a hot melt adhesive. These film materials are delivered to the user in rolled-up form, are then unwound, and thermally activated by the user for bonding to the substrate in the laminating step. However, such films are very expensive and not very convenient, since the user is forced to store various widths of film and the unavoidable waste of film material in cutting the film to size is expensive in view of the high cost of the film material. A typical problem encountered with pre-coated or co-extruded films is edge wrinkling, especially in winding and unwinding rolls of such films. Further, these films exhibit insufficient thermal resistance and tear characteristics.

From U.S.-patents 4,816,306; 4,874,804; 5,500,472; 5,331,033 and from EP 0 721 006 A1, adhesives mainly consisting of ethylene/n-butylacrylate and a variety of tackifying resins, and polymeric waxes are known. These adhesives are exclusively described in these documents as packaging adhesives, especially as case and carton sealing products. The specific characteristics required in a carton sealing adhesive are not related to those required for laminating applications.

Typical further prior art publications in the field include EP 707 054; JP 05302067; JP 03182322; JP 01317756; JP 1259938; JP 60232949; US-4,373,066; US-4,337,298; US 5,532,053 and US 4,576,865.

In general, hot melt adhesives are used in continuous web processes. It is an object of the invention to provide a new method of laminating a laminating material, such as, especially, a transparent laminating film material, to a substrate, especially a printed paper or cardboard substrate, which avoids the above-mentioned disadvantages of prior art laminating adhesives.

It is another object of the invention to provide such a method which is easy and inexpensive to operate, and combines the advantages of in-line adhesive application to the film and/or the substrate with the advantages of pre-coated heat-sealable film materials, at the same time avoiding most or all of the disadvantages of these prior art methods.

It is another object of the invention to provide adhesives which are suitable for operating this method.

It is a further important object of this invention to provide "100%" hot melt adhesives which can be applied in-line, more or less immediately before the laminating

step, to produce transparent, high-gloss film laminations.

According to the invention, these objects are solved by a method of laminating a laminating material, especially a
5 laminating film material, onto a substrate with a hot melt adhesive, by in-line coating said hot melt onto said laminating material and/or said substrate at or above the lowest processing temperature of said hot melt, before laminating the laminating material onto said substrate,
10 said hot melt adhesive comprising up to 100% of a thermoplastic polymer selected from copolymers of olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters;
15 copolymers of olefins, especially ethylene, and vinylic compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene;
20 ionomers and corresponding copolymers; and mixtures thereof.

A hot melt suitable for solving these objects, especially in the context of the invention's method, comprises the
25 following components: up to 100 % of a thermoplastic polymer selected from copolymers of olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters; copolymers of
30 olefins, especially ethylene, and vinylic compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene; ionomers
35 and corresponding copolymers; and mixtures thereof; 0-50 % aliphatic hydrocarbon resin; 0-20 % aromatic hydrocarbon resin; 0-40% rosin and 0-20% wax, said components and

their amounts being chosen so that the adhesive is in-line coatable onto a laminating material and/or a laminating substrate, for subsequent in-line lamination of said laminating material onto said substrate.

5

Hot melt adhesives based on ethylene/n-butyl-acrylate and ethylene/methylacrylate copolymers are especially preferred.

- 10 In a preferred embodiment, the substrate to be laminated is paper or cardboard, especially printed paper, processed photographic paper or printed cardboard, as used in the production of e.g. book-covers, picture postcards, calendars, posters, high quality packaging materials and
- 15 gift-wraps, etc. The laminating material can be synthetic film material, paper, textile material or any other flexible laminating material suitable for lamination; preferably, the laminating material is, however, a synthetic film material, especially a clear and transparent film
- 20 material as is customarily used for such laminations.

- Typically such film materials comprise plane or embossed films, which are at least substantially made from oriented polypropylene, polyethylene, polyester, polyacetate,
- 25 nylon, and other such materials. Mixtures of such polymer, and films consisting of more than one such film material by co-extrusion or other such methods can be used.

- In the presently most preferred embodiment of the invention, the hot melt is in-line coated onto the film material, more or less immediately before the substrate and the film material are adhered to each other in the laminating machine. For this purpose, the hot melt is supplied by customary apparatuses to a suitable coating
- 35 device, preferably located sufficiently close to the film material for directly coating the hot melt onto the film. Generally, the hot melt will be thermally made flowable in

a suitable tank or reservoir, and will be pumped or otherwise conducted in flowable form to the coating device. The coating device is preferably a slot nozzle. It is often advantageous to keep the slot nozzle in direct contact
5 with the film material for coating. The amounts of hot melt coated onto the film material will generally be between 0.5 and 20 g/m². Suitable machines are e.g. described in German patent application 195 46 272.6, not published at the filing date of this application.

10 It is possible to coat the hot melt onto the substrate instead of the laminating material. For specific applications, it can be advantageous to coat the hot melt both onto the substrate and the laminating material. It is of
15 course possible to use other coating devices than slot nozzles for operating the inventive method, and in fact, any device or technique can be used to coat the adhesive onto the laminating material and/or the substrate, as long as the required amount of adhesive is applied in the
20 necessary areas of the laminating material and/or substrate.

Generally, the inventive method will be operated so that unnecessary thermal exposure of the laminating materials,
25 including the hot melt, is avoided. The processing and handling temperatures before, during and after lamination will be selected so that deterioration of materials under the influence of heat is avoided as much as possible. To achieve this, the hot melt will be preferably heated only
30 so much as to make its supply to the coating device and the subsequent coating onto the laminating material and/or the substrate possible. Therefore, while the hot melt must be at or above its lowest processing temperature for coating and lamination, its temperature will be kept close
35 to the lowest processing temperature. It will often be possible to laminate the film onto the substrate substantially without much further heating after the coating

step. It will generally be sufficient to let the laminated product cool to ambient temperatures without taking any measures to accelerate this cooling process. In some cases, it may, however, be advantageous to actively cool the laminated product, e.g. by blowing cold air onto the product leaving the laminating stage.

For practising the method of this invention, hot melts are used which comprise a thermoplastic polymer selected from copolymers of olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters; copolymers of olefins, especially ethylene, and vinyl compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene; ionomers and corresponding copolymers; and mixtures thereof. The presently most preferred such thermoplastic polymers substantially or completely consist of one or more ethylene/methylacrylate copolymers (EMA's) and/or ethylene/n-butylacrylate copolymers (EnBA's). EnBA copolymers are presently the most preferred such polymers.

EMA and EnBA copolymers are e.g. available from Elf Atochem, under the Lotryl® tradename, and from Quantum Chemical Co. and from Exxon Chemical Co. under the Optema-tradename. A variety of different grades of EMA and EnBA copolymers are available; they mainly differ in ester content, melt flow index (MFI) and melting point.

The hot melt adhesive usable for practising the invention's method can, in the simplest case, consist substantially or even completely of one or more grades of EMA or EnBA copolymer. Handling and application performance, processing temperature and other such parameters of the

hot melt can be adjusted by selecting and blending suitable amounts of different grades of such copolymers.

Generally, the invention's hot melts will, however, additionally comprise one or more tackifying resins, plasticizers and waxes plus, in case, customary additives and adjuvants, such as oils, stabilizers, antioxidants, etc. Thus, a hot melt for in-line coating will often comprise, besides the thermoplastic polymer, an aliphatic and/or aromatic hydrocarbon resin, as a tackifying resin. It is presently preferred to use either aliphatic or aromatic hydrocarbon resin. The preferred aliphatic resins are hydrogenated aliphatic hydrocarbon resins, e.g. resins from the Escorez(TM) 5000 series, available from EXXON, the Arcon P(TM) and/or Arcon M(TM)-range from Arakawa Chemical, and the Regalite(TM) range from Hercules.

As aromatic hydrocarbon resins, α -methylstyrene resins are preferred. These can be obtained from Hercules, under the Kristallex tradename, or from Arizona, under the Uratack tradename.

Rosin and rosin ester, especially hydrogenated rosins, can also be advantageously used as tackifying resin in the context of this invention. Hydrogenated rosins, such as Foral AX(TM) from Hercules are preferred.

It is often advantageous to add other polymers, of various molecular weights, to the invention's hot melt. Thus, in some preferred embodiments of the invention, the hot melt additionally contains polyethylene wax, such as AC 8 from Allied Chemical.

A hot melt laminating adhesive, which can advantageously be used in the context of the inventive method, will thus generally comprise the following components: up to 100 % of a thermoplastic polymer selected from copolymers of

olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters; copolymers of olefins, especially ethylene, and vinylic compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene; ionomers and corresponding copolymers; and mixtures thereof; 0-50 % aliphatic hydrocarbon resin; 0-20 % aromatic hydrocarbon resin; 0-40% rosin and 0-20% wax, said components and their amounts being chosen so that the adhesive is in-line coatable onto a laminating material and/or a laminating substrate, for subsequent in-line lamination of said laminating material to said substrate.

More preferably, the adhesive will comprise the following components: up to 100% of at least one EMA and/or EnBA copolymer; 0-50% hydrogenated aliphatic hydrocarbon resin; 0-20% α -methylstyrene resin; 0-40% hydrogenated rosin and 0-20% polyethylene wax.

In presently preferred special embodiments, the hot melt adhesive essentially consists of 35-60% EnBA or EMA, 30-40% hydrogenated aliphatic hydrocarbon resin or about 10% α -methylstyrene resin; 0-30% hydrogenated rosin and 0-10% polyethylene wax, plus small amounts of stabilizer. In some preferred embodiments, the thermoplastic polymer of the hot melt adhesive is a single grade of EnBA copolymer, usually at the low end of the MFI-range, i.e. with MFI less than 10 g/10 min. In other preferred embodiments, the thermoplastic polymer comprises more than one EnBA grade, and in these cases, the two different grades of EnBA preferably have MFI's which differ by at least a factor of 4 and up to a factor of 10, i.e. one grade has an MFI more than 4 times that of the other grade.

For some applications, it can be advantageous to use three or even more such different grades of EnBA, with correspondingly different MFI's.

5

The inventive hot melts can be used at application temperatures (or processing temperatures) which are low enough to prevent distortion of heat sensitive plastic film, and at the same time show excellent flow properties at such low temperature. It is e.g. possible to coat and laminate the inventive hot melts at temperatures below 120° C, often between 90° and 120°C, and still ensure even and homogeneous distribution of the hot melt on the laminating materials. Presently, contact coating of the hot melt adhesive onto the film is preferred. It may alternatively be advantageous to use non-contact coating, especially for heat-sensitive films. Excellent film forming performance is achieved, and the laminated products exhibits high glossiness.

20

The laminating adhesives of the invention provide high transparency of the hot melt coating, so that high gloss is achieved, while readability and color rendition of e.g. printing on the substrate is not impaired.

25

The inventive hot melts show high hot-tack and excellent open time characteristics as well as setting properties. They meet the requirements of machine condition, in-line embossing and cutting.

30

Laminates made according to the invention exhibit high heat resistance and high UV-resistance, and correspondingly little delamination or yellowing. Also after heat forming and embossing, no delamination is observed when the hot melt formulations of the invention are used.

35

The following Examples are set forth for purposes of illustration only and are not to be construed to limit the claims in any manner whatsoever.

- 5 Examples of the most preferred formulations are as follows:

Example 1:

	parts
10 Ethylene-acrylic copolymers:	
Lotryl 17 BA 07	23
Lotryl 35 BA 40	15
Lotryl 35 BA 320	17
15 Aliphatic hydrocarbon resin:	
Escorez 5300	28
Rosin:	
Foral AX	10
20 Polyethylene/polyethylene wax:	
AC 8	5
25 Stabilizers	2

Example 2:

	parts
30 Ethylene-acrylic copolymer:	
Lotryl 17 BA 07	40
Aliphatic hydrocarbon resin:	
Escorez 5300	38
35 Rosin:	
Foral AX	10
Polyethylene/polyethylene wax:	
AC 8	10
40 Stabilizers	2

Example 3:

	parts
Ethylene-acrylic copolymer:	
5 Lotryl 17 BA 07	35
Aliphatic hydrocarbon resin:	
Escorez 5300	38
10 Rosin:	
Foral AX	25
Stabilizers	2

15

Example 4:

	parts
Ethylene-acrylic copolymers:	
Lotryl 17 BA 04	10
20 Lotryl 35 BA 40	20
Lotryl 35 BA 320	30
Aliphatic hydrocarbon resin:	
Escorez 5300	38
25 Stabilizers	2

Example 5:

	parts
30 Ethylene-acrylic copolymers:	
Lotryl 17 BA 07	23
Lotryl 35 BA 40	15
35 Lotryl 35 BA 320	17
Aromatic hydrocarbon resin:	
Kristallex F 85	10
Rosin:	
40 Foral AX	28
Polyethylene/polyethylene wax:	
AC 8	5
45 Stabilizers	2

The hot melts of Examples 1-5 were in-line coated onto laminating film in accordance with the inventive method.

For this purpose, the in-line coating apparatus, as disclosed in German patent application P 195 46 272.6 was used. The hot melt was thus applied to the film directly before the film was passed, together with a
5 substrate, between the heated laminating rollers. Excellent high-gloss fully transparent laminations were thus produced.

CLAIMS

1. A method of laminating a laminating material, especially a laminating film material, onto a substrate
5 with a hot melt adhesive, by in-line coating said hot melt adhesive onto said laminating material and/or said substrate, at or above the lowest processing temperature of said hot melt, and laminating the laminating material onto said substrate, said hot melt adhesive comprising a
10 thermoplastic polymer selected from copolymers of olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters; copolymers of olefins, especially ethylene, and vinylic
15 compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene; ionomers and corresponding copolymers; and mixtures
20 thereof.

2. The method of claim 1, the substrate being paper or cardboard, especially printed paper, printed cardboard or processed photographic paper.
25

3. The method of claim 1 or 2, the laminating material being a synthetic film material, especially a clear, transparent film material.

30 4. The method of claim 3, said film material substantially consisting of a plane or embossed synthetic film material selected from oriented polypropylene (OPP), polyethylene (PE), polyester, polyacetate, nylon and mixtures thereof.
35

5. The method according to any one of claims 1 to 4, said hot melt being in-line coated onto said substrate

and/or said laminating material, immediately before the substrate and laminating material are adhered to each other.

- 5 6. The method of claim 5, said hot melt being coated onto said laminating material from a slot nozzle at a coating amount between 0.5 and 20 g/m².

7. The method of claim 1, 3 or 5, wherein said
10 thermoplastic polymer substantially consists of one or more ethylene/methylacrylate copolymers (EMA's) and/or ethylene/n-butylacrylate copolymers (EnBA's).

8. The method of claim 7, wherein said hot melt
15 additionally comprises one or more tackifying resins, plasticizers and waxes, and, in case, customary additives and adjuvants such as oils, stabilizers and antioxidants.

9. The method of claim 8, wherein the tackifying
20 resin is selected from aliphatic and aromatic hydrocarbon resins, especially hydrogenated aliphatic hydrocarbon resins and α -methylstyrene resins, and rosins and rosin-esters, especially hydrogenated rosins and rosin esters.

- 25 10. The method of claim 9, said hot melt additionally containing at least one further polymer, especially a polyolefins such as polyethylene or a polyethylene wax.

11. The method of any one of claims 1 to 10, said hot
30 melt essentially consisting of

preferably more preferred

- | | | | | |
|----|---------------------------------------|---------|--------|--------|
| | -thermoplastic (co)-
polymers | 10-100% | 20-80% | 35-60% |
| 35 | - aliphatic hydrocar-
bon resin(s) | 0- 50% | 0-45% | 0-40% |
| 40 | - aromatic hydrocar-
bon resin(s) | 0- 20% | 0-15% | 0-10% |

16

-rosin(s)	0- 40%	0-35%	0-30%
- polyethylenes/ polyethylene waxes	0- 20%	0-15%	0-10%

5

and, in case, small amounts of customary additives and adjuvantes.

12. A hot melt laminating adhesive comprising the following components:

- up to 100 % of a thermoplastic polymer selected from copolymers of olefins, especially ethylene, and (meth-)acrylic acid; copolymers of olefins, especially ethylene, and (meth-)acrylic acid derivatives, especially (meth-)acrylic acid esters; copolymers of olefins, especially ethylene, and vinylic compounds, especially vinyl carboxylates such as vinyl acetate; poly- α -olefins, especially atactic poly- α -olefins (APAO's); thermoplastic rubbers; metallocene-catalyzed polymers, especially based on ethylene and/or propylene; ionomers and corresponding copolymers; and mixtures thereof;
- 0-50 % aliphatic hydrocarbon resin;
- 0-20 % aromatic hydrocarbon resin;
- 0-40% rosin and

0-20% wax,

said components and their amounts being chosen so that the adhesive is in-line coatable onto a laminating material and/or a laminating substrate, for subsequent in-line lamination of said laminating material onto said substrate.

13. The adhesive of claim 12, comprising the following components:

- up to 100% of at least one EMA and/or EnBA copolymer;
- 0-50% hydrogenated aliphatic hydrocarbon resin;
- 0-20% α -methylstyrene resin;
- 0-40% hydrogenated rosin and
- 0-20% polyethylene wax.

14. The adhesive of claim 13, essentially consisting of

35-60% EnBA or EMA;

5 30-40% hydrogenated aliphatic hydrocarbon resin or about 10% α -methylstyrene resin;

0-30% hydrogenated rosin and

0-10% polyethylene wax,

plus small amounts of stabilizer.

10

15. The adhesive of claim 13 or 14, wherein the thermoplastic polymer component comprises more than one EnBA grade, said grades differing in ester content, melt flow index (MFI) and/or melting point.

15

16. The adhesive of claim 15, comprising at least two different grades of EnBA, one of said grades having an MFI (in g/10 min) at least 4 times and up to 10 times higher than that of the other grade.

20

17. The adhesive of claim 16, comprising at least three different such grades of EnBA.

25

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 96/04359

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B32B31/30 B32B27/10 C09J123/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B32B C09J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 85 01052 A (DOW CHEMICAL CO) 14 March 1985 see page 5, line 11 - page 6, line 3; claims 1-5,10; example 3 ---	1-14
X	US 3 862 869 A (PETERSON LENART A ET AL) 28 January 1975 see column 2, line 43 - line 50 see column 3, line 59 - column 4, line 10; figure 2 ---	1-6,11, 12
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 374 (M-1293), 11 August 1992 & JP 04 119839 A (HONSHU PAPER CO LTD), 21 April 1992, see abstract; figures 7,10 --- -/--	1,2,5,6, 11,12
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 17 June 1997		Date of mailing of the international search report 27. 06. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2200 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer Van Nieuwenhuize, O

INTERNATIONAL SEARCH REPORT

International Application No.

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C/(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 078 168 A (GRACE W R & CO) 6 January 1982 see claim 21 ---	1,3-6, 11,12
X	EP 0 592 920 A (TETRA LAVAL HOLDINGS & FINANCE) 20 April 1994 see figure 1 ---	1,2,5,6, 11,12
X	EP 0 547 798 A (MINNESOTA MINING & MFG) 23 June 1993 see page 6, line 29 - page 8, line 4 see page 8, line 29 - line 34 see page 14, line 30 - line 36; claims 1-3,5; examples 29-32 ---	1,5,7-14
X	EP 0 547 797 A (MINNESOTA MINING & MFG) 23 June 1993 see page 9, line 19 - line 55; claims 1-3 ---	1,5,7-12
X	EP 0 300 158 A (NAT STARCH CHEM CORP) 25 January 1989 cited in the application see claims 1,10; examples 1,2 ---	12-17
X	EP 0 721 006 A (NAT STARCH CHEM INVEST) 10 July 1996 cited in the application see the whole document ---	12-17
X	EP 0 474 412 A (DU PONT) 11 March 1992 see claims 1-8 ---	12-15
E	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 309947 A (SUMITOMO CHEM CO LTD) see abstract ---	12,13
A	WO 95 00333 A (AMERICAN NATIONAL CAN CO) 5 January 1995 see claim 1; examples 22-24 ---	1
A	WO 95 01250 A (DOW CHEMICAL CO) 12 January 1995 see claims 1,13-16 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/04359

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8501052 A	14-03-85	AU 3249984 A BR 8407048 A EP 0140019 A JP 60501864 T US 4631308 A	07-03-85 30-07-85 08-05-85 31-10-85 23-12-86
US 3862869 A	28-01-75	US 3752732 A	14-08-73
GB 2078168 A	06-01-82	BE 888683 A CH 652650 A DE 3115954 A FR 2484913 A GB 2143173 A,B NL 8102058 A SE 451311 B SE 8102594 A	28-08-81 29-11-85 28-01-82 24-12-81 06-02-85 18-01-82 28-09-87 24-12-81
EP 0592920 A	20-04-94	AT 139479 T DE 69303246 D DE 69303246 T ES 2088208 T JP 6226851 A	15-07-96 25-07-96 31-10-96 01-08-96 16-08-94
EP 0547798 A	23-06-93	CA 2083005 A JP 5255548 A	18-06-93 05-10-93
EP 0547797 A	23-06-93	US 5310803 A CA 2084226 A JP 5239285 A	10-05-94 18-06-93 17-09-93
EP 0300158 A	25-01-89	US 4816306 A CA 1331817 A DE 3883106 A DE 3883106 T US 4874804 A	28-03-89 30-08-94 16-09-93 02-12-93 17-10-89
EP 0721006 A	10-07-96	AU 4079596 A CA 2166497 A JP 8231935 A	29-08-96 07-07-96 10-09-96

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/04359

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0474412 A	11-03-92	US 5373041 A	13-12-94
		CA 2049746 A	28-02-92
		DE 69107550 D	30-03-95
		DE 69107550 T	21-09-95
		JP 4233986 A	21-08-92
		JP 7005872 B	25-01-95

WO 9500333 A	05-01-95	AU 7211894 A	17-01-95
		EP 0706455 A	17-04-96
		JP 9502401 T	11-03-97

WO 9501250 A	12-01-95	US 5395471 A	07-03-95
		CA 2165191 A	12-01-95
		EP 0706448 A	17-04-96
		FI 956302 A	28-12-95
		JP 8512002 T	17-12-96
		US 5582923 A	10-12-96
